Applied Catalysis B: Environmental 146 (2014) 274–278

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Environmental-friendly strategy for biocatalytic conversion of waste glycerol to glycerol carbonate

Madalina Tudorache[a], Alina Negoi[a], Bogdan Tudora[b], Vasile I. Parvulescu[a,*]

[a] University of Bucharest, Department of Organic Chemistry, Biochemistry and Catalysis, Bd. Regina Elisabeta 4-12, Bucharest 030016, Romania
[b] Central Customs Laboratory, National Customs Authority, Street Vulturilor, no. 2, Bucharest 030855, Romania

ARTICLE INFO

Article history:
Received 30 October 2012
Received in revised form 15 February 2013
Accepted 19 February 2013
Available online 4 March 2013

Keywords:
Waste glycerol
Biocatalysis
Glycerol carbonate
Solvent-free system
Impurity

ABSTRACT

In this work, the conversion of waste glycerol from biodiesel production to glycerol carbonate (GlyC) as added-value product has been investigated. The transformation of waste glycerol to GlyC has been achieved taking the advantage of dimethyl carbonate (DMC) reaction with glycerol catalyzed by heterogeneous lipase biocatalyst under solvent-free conditions. The biocatalyst design was the lipase enzyme anchored on magnetic nano-particle surface *via* covalent binding. Waste glycerol with different matrixes according to the feedstock patterns (*e.g.* soybean, sunflower, rape, corn, olive, palm, and residual oil) has been tested for GlyC bio-synthesis. Content of MeOH, H_2O, metals and salts from sample matrix (*e.g.* waste glycerol) was characterized using gravimetric and energy dispersive X-ray fluorescence (EDXRF) spectrometry techniques. Impurities effects of the waste glycerol on the performance of the biocatalytic process and also different strategies to avoid them were investigated.

1. Introduction

Worldwide production of biodiesel has been well developed and the biodiesel process became one of the promising alternative as renewable fuels in recent years [1,2]. The main co-product of biodiesel process (10%, w/w) is glycerol regardless of the biomass source (*e.g.* mustard, rapeseed, canola, corn, soybean, sunflower and waste cooking oils). Every 100 kg of biodiesel generates around 10 kg of glycerol. A surplus of glycerol in the future will impact on the economic and environmental aspects of the biodiesel viability. Despite the pure glycerol has numerous industrial applications the use of glycerol derived from the biodiesel production is highly limited due to its composition [3].

Crude glycerol as waste stream of biodiesel production possesses low value because of its impurities (*e.g.* catalyst, residual methanol, water, salts, soap and free fatty acids) [4]. Chemical composition of waste glycerol mainly varies with the biodiesel process (*i.e.* type of the catalyst and chemical route used to produce biodiesel) and the parent feedstock. Transesterification with methanol catalyzed by homogeneous alkaline catalysts provides a waste glycerol with a broad variation of composition (30–96 wt% of glycerol, and 5–7 wt% salts) [2]. The methanol content is directly correlated to the catalyst efficiency. Heterogeneous catalysts based on enzymes or metal oxides represent alternatives for improving the quality of waste glycerol [1]. However, even using such routes the impurities of the natural feedstock are accumulated in the glycerol phase providing a considerable impure composition of waste glycerol.

Impurities of waste glycerol can strongly influence the glycerol conversion into requested products. The impurities can inhibit the cell growth for biological processes or poison the catalyst in conventional catalytic reactions [5]. Therefore, the purification of waste glycerol is required in order to yield a commercial grade compound. Filtration, chemical additions, and fractional vacuum distillation are common operations for the purification of crude glycerol but they request additional steps and lead to an increase of the procedure cost. If it is used in food, cosmetics or drugs, further purifications for removing impurity traces are needed such as bleaching, deodorizing and ion exchange [6].

In the last years, several strategies were proposed to convert both the raw glycerol and waste glycerol to value-added products based on chemical and biochemical transformations [7]. They include the use of unrefined glycerol such as animal feed, or for co-digestion and co-gasification while the waste glycerol for the synthesis of chemical products, production of hydrogen, development of fuel cell, production of ethanol, methanol or 1,2-propanediol, oxidation, synthesis of acrolein, *etc.* [7–13]. However, most of the reports refer to the use of pure glycerol poisoned with impurities (*i.e.* pure glycerol artificial mixed with supposed impurities). Only few reports were focused on the use of real waste glycerol from biodiesel industry. In most of these cases the glycerol

* Corresponding author. Tel.: +40 21 4100241; fax: +40 21 4100241.
E-mail addresses: vasile.parvulescu@g.unibuc.ro, v_parvulescu@yahoo.com (V.I. Parvulescu).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.02.049

conversion was based on biotransformation. As examples, acrolein was produced by raw glycerol fermentation [14], 1,3-propanediol by anaerobic fermentative production in fed-batch cultures of *Klebsiella pneumonia* or *Clostridium butyricum* [15–17], citric acid by fermentation with *Yarrowia lipolytica* mutant cell [18], hydrogen and/or ethanol by photo-fermentative conversion in the presence of bacterium *Rhodopseudomonas palustris* [19,20], and polyesters and biosurfactants by bacterial digestion [21,22].

In this paper we report the use of waste glycerol for biocatalytic synthesis of glycerol carbonate (GlyC) as a value-added product with numerous applications in chemical industry (*e.g.* component of gas-separation membranes, "green" (non-volatile) solvent for dyes, lacquers, detergents, adhesives and cosmetics, intermediate for the production of resins and plastics, electrolyte ingredient of lithium-based batteries, and precursor in biomedical applications) [6,23]. The biocatalytic route used for GlyC synthesis consists in the reaction between glycerol and dimethyl carbonate (DMC) catalyzed by a lipase-linked on magnetic nano-particles. The biocatalyst designed as a covalently attached enzyme lipase onto the magnetic nano-particle surface was selected for GlyC synthesis based on our previous results and literature information [24–27]. Immobilized *Aspergillus niger* lipase on the nano-magnetic particles was preferred to the free enzyme due to its higher stability and recyclability under experimental conditions (*i.e.* fifteen cycles for immobilized enzyme and only four cycles for free enzyme) [25,26]. Also, the immobilized lipase demonstrated higher efficiency (45% glycerol conversion after 6 h reaction time) than immobilized *Candida antarctica* lipase on resin (60% glycerol conversion after 50 h reaction time) under similar GlyC synthesis conditions (1:10 = glycerol:DMC and 60 °C).

This paper reports an environmental-friendly strategy considering solvent-free conditions (set up in our previous report) [26] and waste glycerol collected from different feedstock patterns (*e.g.* soybean, sunflower, rape, corn, olive, palm, and residual oil). The effects of the matrix impurities on the GlyC bio-synthesis were also investigated.

2. Experimental

2.1. Chemicals and solutions

Standard glycerol and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich (USA). The lipase from *A. niger* source (Sigma–Aldrich, USA) was immobilized on the surface of magnetic nano-particles (50 nm external diameter and polyethylenamine coverage with $-NH_2$ terminal groups) provided from Chemicell, Rostock, Germany. All the synthesis reagents were purchased from Sigma–Aldrich (USA). Derivatization reagents (*BSTFA* - N,O-bis(trimethylsilyl) trifluoroacetamide, TMCS - trimethylchlorosilane (BSTFA:TMCS = 99:1) and pyridine) were purchased from Macherey-Nagel Corp. (Duren, Germany) and Fluka (Switzerland). The organic solvents used in all the experiments were of the analytic purity.

2.2. Waste glycerol pre-treatment

Waste glycerol was the glycerol prepared from different oils (*e.g.* residual, soybean, sunflower, rape, corn, olive, and palm oils) using a reported biodiesel procedure [28]. Rape and corn oils were of industrial purity (unrefined oils), while the others were refined oils (*e.g.* residual, soybean, sunflower, olive, and palm oils). Glycerol from residual sun-flower oil recovered from the cooking process was used as well.

Before the biocatalytic experiments, waste glycerols were treated in different steps. Firstly, they were heated at 120 °C (15 min) for the evaporation of methanol and water. Then they were diluted with distilled water (glycerol:water ratio of 1:4) to decrease the sample viscosity. In order to eliminate the fatty acids, the pH value has been adjusted to acidic one (pH 3–4) by titration with HCl. The precipitated fatty acids were then separated by centrifugation (6000 rpm, 5 min).

Also, glycerols were mixed with silica particles in equal mass proportion (1:1). In this way, all hydrophilic content of the waste glycerol was adsorbed by silica material.

2.3. Characterization of waste glycerol content

Waste glycerol samples were analyzed based on the energy dispersive X-ray fluorescence (EDXRF) spectrometry technique in order to determine the metals and salts composition of the matrices. In this scope, the waste glycerol was diluted with distilled water (sample:H_2O ratio of 2:7). The diluted sample was analyzed with the elemental analyzer spectrometer EDXRF (X-Calibur - Xenemetrix, Migdal Haemek, Israel) looking for Na, K, Mg, Ca, P and S content.

Methanol (MeOH), water and fats composition of the waste glycerol were determined using gravimetric technique. Weight loss of the samples after the acidification (pH 3–4) and centrifugation was assigned as fats content. Similarly, MeOH and H_2O percents of the waste glycerol were calculated as the difference between the sample mass before and after evaporation at 60 °C and 120 °C, respectively.

2.4. Biocatalytic synthesis of GlyC

Waste and standard glycerol were used as substrate for biocatalytic synthesis of GlyC. Enzymatic synthesis of GlyC has been performed in solvent-free system. Given amounts of Gly and DMC (Gly:DMC molar ratio of 1:10) were mixed together with the lipase-magnetic particle biocatalyst (5%, w/w) in a 1.5 mL reaction vial (Eppendorf tube). The protocol of biocatalyst preparation was reported in our previous paper [26]. The mixtures were incubated for 6 h under stirring at 60 °C using a thermostated shaker. Then, the biocatalyst was recovered from the reaction mixture separating the lipase-magnetic particles with a permanent magnet from the liquid phase. The reaction mixture without biocatalyst was proper pre-treated (100 μL silylation agent BSTFA:TMCS = 99:1 and 100 μL pyridine) for gas chromatography (GC) coupled to flam ionization (FID) detection (Schimadzu GC-2014, Thermo Electron Scientific Corporation, USA). The performances of the biocatalytic system were evaluated based on the GlyC yield calculated as the ratio of GlyC synthesized in the reaction (from the GC chromatogram) to the theoretical one.

3. Results and discussion

3.1. Effects of MeOH and water on GlyC synthesis

Waste glycerol from biodiesel production contained many impurities, such as methanol, water, fatty acids, salts, metals, *etc.* [4]. MeOH and soaps are usually the dominant impurities. Obviously MeOH is used in a large excess in transesterification of fatty esters. On the other side the alkaline catalyst (NaOH or natrium methoxide) is reacting with the free fatty acids of the feedstock leading to soaps. Both impurities are soluble in the aqueous phase containing glycerol [2]. The soap was found to exhibit no effect on the biocatalytic reaction.

To investigate the effect of MeOH, standard glycerol was mixed with given amounts of MeOH for miming the real matrix of waste glycerol. Experimental data are shown in Fig. 1. The presence of MeOH inhibited dramatically the GlyC yield. Only 2% of MeOH in

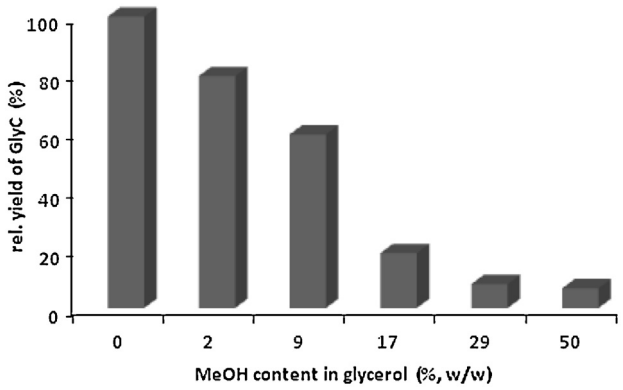


Fig. 1. Effect of MeOH impurity on GlyC synthesis. Conditions of GlyC synthesis: 25 mg glycerol sample, 0.5 mL DMC, 5% lipase-linked magnetic nano-particles, 60 °C temperature and 6 h incubation time.

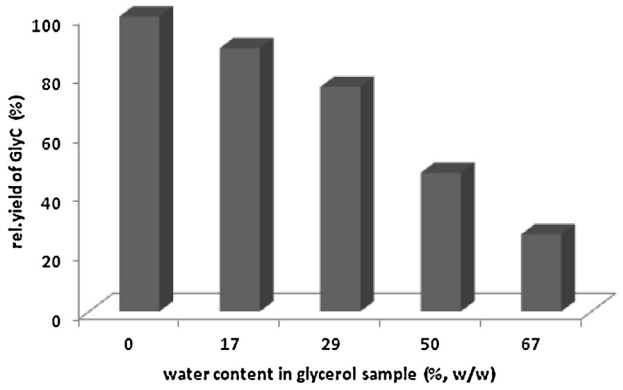


Fig. 2. Effect of H_2O impurity on GlyC synthesis. Conditions of GlyC synthesis: 25 mg glycerol sample, 0.5 mL DMC, 5% lipase-linked magnetic nano-particles, 60 °C temperature and 6 h incubation time.

glycerol sample caused a decrease with around 20% of the yield in GlyC. Regressive tendency of process performance was determinate for more MeOH addition (Fig. 1). The biocatalytic process was almost suppressed for 29% of MeOH in glycerol sample.

The presence of MeOH in the glycerol sample generated a cumulative effect. MeOH impurity affected the catalytic capacity of the lipase enzyme that is not complicate to be explained taking into consideration that the proteins are unstable in the presence of short-chain alcohols [29]. An additional MeOH is produced during the synthesis of GlyC (Scheme 1). The reaction of glycerol with DMC is generating an unstable intermediate and MeOH. Intermolecular cyclization allows the stabilization of the product concomitantly with the production of a second MeOH molecule [26].

Effect of water was tested in a similar way with that used for MeOH by mixing given amounts of water with standard glycerol. Fig. 2 shows the GlyC yield obtained for different percents of water in glycerol samples (*e.g.* 17, 29, 50 and 67%). GlyC yield decreased slightly with water composition leading for 17 wt% H_2O to a 11% inhibition of the GlyC yield. Stronger effects appeared for water

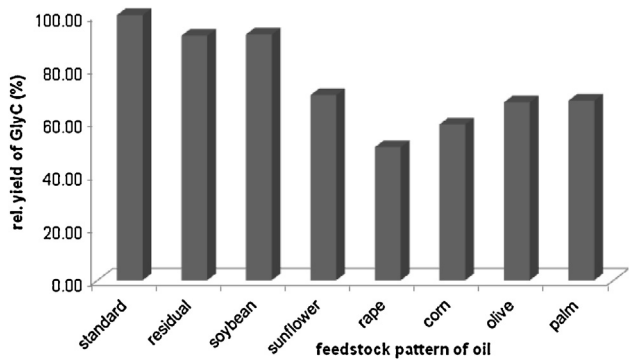


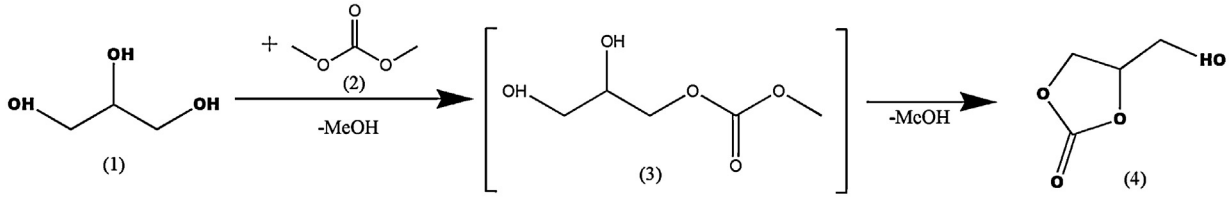
Fig. 3. Influence of waste glycerol composition on GlyC synthesis. Conditions of GlyC synthesis: 25 mg glycerol sample, 0.5 mL DMC, 5% lipase-linked magnetic nano-particles, 60 °C temperature and 6 h incubation time.

contents higher than 30 wt%. Thus, the yield to GlyC was reduced to half for a water content of 50 wt%, while 67 wt% H_2O corresponded to a decrease of 70% yield (Fig. 2). High water contents in the reaction environment inhibited the lipase activity, because the lipase enzyme requested preponderantly a hydrophobic environment [30]. However, the presence of water in traces (hydrophilic phase) is imposed in order to conserve the spatial enzyme structure [31]. On the other hand, GlyC itself is unstable in the presence of water.

3.2. Waste glycerol on GlyC synthesis

The waste glycerol obtained from the transesterification of soybean, sunflower, rape, corn, olive, palm, and residual oil was further utilized in GlyC synthesis. Fig. 3 shows the yields in GlyC from these sources. It indicates that under identical reaction conditions the nature of the fatty ester precursor is important. The higher yields were obtained from residual and soybean oils, where around 95% from the maximum GlyC yield were recovered. Glycerol from other sources led to smaller yields. Sunflower, olive and palm oils led to around 70% from the maximum GlyC yield while the lowest conversion was obtained for samples derived from rape and corn.

The key aspect of the waste glycerol behavior was the sample composition (*i.e.* matrix of waste glycerol). Chemical composition of waste glycerol samples determined taking into consideration the content in MeOH, water, soaps, metals (Na, K, Ca and Mg) and salts (P for phosphates and S for sulfates) is presented in Table 1. These date correlate very well with the yields presented in Fig. 3. The best performances correspond to a lower MeOH content (*e.g.* 6.5 and 6.2% MeOH for residual and soybean oil, respectively) that is also in a good concordance with previous reports [2]. Waste glycerol from palm oil had also a low MeOH content (*e.g.* 6.2% MeOH) but in that case the water content was higher 36.3% that led to a cumulative inhibition effect on the lipase enzyme diminishing the processes efficiency. Waste glycerol from rape and corn contained higher MeOH amount (*e.g.* 13.9 and 11.3% MeOH for rape and corn, respectively), which dramatically affected the efficiency of GlyC synthesis according to Fig. 3. Metal ions like sodium, potassium



Scheme 1. Reaction of GlyC synthesis. (1) glycerol, (2) dimethyl carbonate (DMC, (3) unstable intermediate and (4) glycerol carbonate (GlyC).

Table 1
Chemical composition of waste glycerol from biodiesel production.

Raw material for biodiesel	Methanol (%)	Water (%)	Soap (%)	Calcium	Phosphorus	Sulfur
Residual oil	6.5	29.8	<1	Yes	–	Yes
Soybean oil	6.2	26.5	<1	–	–	–
Rape oil	13.9	24.5	<1	Yes	–	–
Sunflower oil	2.9	28.8	<1	–	Yes	Yes
Corn oil	11.3	13.6	<1	Yes	–	–
Olive oil	8.9	47.1	<1	Yes	Yes	-
Palm oil	6.2	36.3	<1	–	–	–

Na, Mg and K were not detected in the samples. Corn oil contained Mn (0.1 mg/L).

and magnesium which could affect the lipase activity [32] were not detected in these samples (Table 1) based on high efficiency of heterogeneous transesterification process of biodiesel production [28]. Calcium anions were detected in most of the samples (Table 1), as well as phosphates (phosphorus) and sulfates (sulfur) salts determined in sun-flower and olive matrix do not affect the biocatalyst activity [33]. Surprisingly, manganese was identified in the waste glycerol from corn oil, which provided another reason for the low GlyC yield (Fig. 3).

Biocatalyst robustness was studied in the GlyC production using waste glycerol from all of the feedstock patterns used in the previous experiments (*e.g.* soybean, sunflower, rape, corn, olive, palm, and residual oil). As a general remark, the GlyC yield was enhanced with 20–50% after the first two-three cycles. Then, the catalytic capacity of the biocatalyst was preserved within the next tenth reaction cycles. It was presumed that the improvement of the biocatalyst performance is due to the removal of superficial enzyme molecules kept by protein-protein interactions on the biocatalyst surface. Soap impurities of the waste glycerol (Table 1) act as surfactants and breakdown the enzyme-enzyme interactions allowing the removal of the unspecific enzyme molecules stocked on the biocatalyst surface. In this way, more catalytic sites were accessible. The other impurities of the glycerol matrix did not affect the biocatalyst.

The recovered biocatalyst was characterized using FTIR technique (Fig. SI – supplementary data). All of the spectra have similar profiles with the specific band of the lipase enzyme at 1063 cm^{-1}. This is a clear evidence for the robustness of the biocatalyst during successive cycles and against the waste glycerol impurities.

3.3. Strategies for waste glycerol treatment

Frequently, the use of "crude" glycerol in a chemical and even more in a biochemical process causes the depreciation of the process performance. Therefore, a pretreatment is compulsory in most of the cases. In our experiments, the waste glycerol was also treated in order to diminish the impurities content with consistent influence on GlyC synthesis (*e.g.* MeOH and water).

For this scope several strategies were investigated (Fig. 4). The following protocols were considered: centrifugation (S_1), evaporation (S_2) and centrifugation followed by evaporation (S_3). In addition, waste glycerol mixed with hydroscopic silica particles was tested as substrate for GlyC synthesis. The experimental results are presented in Fig. 4. As a general observation, except for the corn and rape oil samples no improvement has been determined in the biocatalytic synthesis of GlyC. Centrifugation protocol (S_1) applied to waste glycerol affected the GlyC synthesis, and led to lower GlyC yields compared to the reference (standard glycerol) (Fig. 4). However, two exceptions were identified, *i.e.* using corn and rape oils (Fig. 4). The decrease of the GlyC yields could be generated by the loss of glycerol during the centrifugation of waste glycerol. These exceptions could be explained on the basis that both oils were of industrial purity (unrefined oil), while the others (*e.g.* residual, soybean, sunflower, olive and palm oil) were refined oils. The centrifugation step allowed the separation of the solid residues from the oils matrix, which provoked interferences in the GlyC synthesis.

The evaporation protocol (S_2) was applied for the elimination of MeOH and water content from the matrix of the waste glycerol. Again, the pre-treatment led to better yields compared to un-treated oils only for the rape and corn oils (Fig. 4). The efficiency of the process was not affected for residual and palm oil cases, while the GlyC yield decreased slightly for soybean, sunflower and olive oils. Rape and corn oils had the highest MeOH content (Table 1), which inhibited considerably the biocatalytic process. This disadvantage was eliminated using the S_2 protocol and GlyC yield increased from 15.4% to 35.8% for rape oil and from 20.4% to 25.6% for corn oil (Fig. 4). For the other oils, S_2 imposed preponderantly the elimination of the water content since this impurity was dominant compared to MeOH (Table 1). Accordingly, the changes induced by the glycerol matrix were not substantial.

The protocol S_3 is a combination of protocols S_1 and S_2. Consequently, the results reflect this combination (Fig. 4).

In the case of protocol S_4, waste glycerol was mixed with scavenger particles. The expected result was the elimination of the aqueous and MeOH phase and, finally, an improvement of the efficiency of the GlyC synthesis. In fact, the results show unmodified yield of GlyC for sunflower, rape and corn oils, and a decreased GlyC yield for the other oils (Fig. 4). The failure of this protocol was due

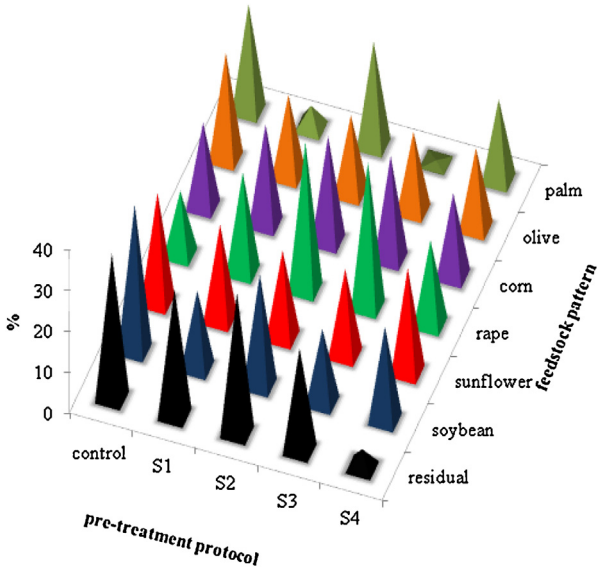


Fig. 4. Effect of the pre-treatment protocol applied to waste glycerol on GlyC synthesis (control – waste glycerol was used in GlyC synthesis without any pretreatment; S_1 – centrifugation of waste glycerol before its use to GlyC synthesis; S_2 – evaporation of waste glycerol before its use to GlyC synthesis; S_3 – centrifugation and evaporation of waste glycerol before its use to GlyC synthesis; S_4 – mixing of waste glycerol with silica particle before its use to GlyC synthesis). Conditions of GlyC synthesis: 25 mg glycerol sample, 0.5 mL DMC, 5% lipase-linked magnetic nano-particles, 60 °C temperature and 6 h incubation time.

to the fact the glycerol is easily adsorbed onto silica together with impurities leading to the limitation of its interaction with DMC.

4. Conclusions

Waste glycerol has been successfully converted to GlyC after the reaction with a DMC excess catalyzed by a lipase heterogeneous catalyst. Experimental results showed that the reaction was sensitive to impurities content of waste glycerol (*e.g.* MeOH and water). The impurities effects were confirmed by experiments with crude waste glycerol. From our knowledge, it is the first time when waste glycerol (unrefined/crude glycerol) is used as raw material (substrate) for GlyC synthesis.

Different strategies (*e.g.* S_1, S_2, S_3 and S_4) for the pre-treatment of the waste glycerol were investigated in order to improve the performances in its bio-conversion to GlyC. The effects of the pre-treatment protocols were indeed significant for waste glycerols with high contents in MeOH (*e.g.* rape and corm oils). This demonstrates one more the inhibition effect of MeOH on the catalytic activity of the lipase. As a general remark, the pre-treatment protocol for waste glycerol has to be chosen empirically according with the impurity content of the sample matrix.

Acknowledgement

This work was financially supported by PN II HR YT-96 program, contract no. 91/2010 from CNCSIS.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.02.049.

References

[1] F. Yang, M.A. Hanna, R. Sun, Bitechnology and Biofuels 5 (2012) 1–10.
[2] J.C. Thompson, B. He, Applied Engineering in Agriculture 22 (2006) 261–265.
[3] M. Dasari, Feedstuffs 79 (2007) 1–3.
[4] S. Hu, X. Luo, C. Wan, Y. Li, Journal of Agricultural and Food Chemistry 60 (2012) 5915–5921.
[5] S. Sattayasamitsathit, P. Methacanon, P. Prasertsan, Electronic Journal of Biotechnology 14 (6) (2011).
[6] M. Pagliaro, M. Rossi, The Future of Glycerol, 2nd ed., The Royal Society of Chemistry, 2010.
[7] A.B. Leoneti, V. Aragão-Leoneti, S.V.W.B. de Oliveira, Renewable Energy 45 (2012) 138–145.
[8] S. Demirel, K. Lehnert, M. Lucas, P. Claus, Applied Catalysis 70 (2007) 637–643.
[9] P. Lauriol-Garbey, G. Postole, S. Loridant, A. Auroux, V. Belliere-Baca, P. Rey, J.M.M. Millet, Applied Catalysis B: Environmental 106 (2011) 94–102.
[10] Z. Yuan, J. Wang, L. Wang, W. Xie, P. Chen, Z. Hou, et al., Bioresource Technology 101 (2010) 7088–7092.
[11] B.R. Sereshki, S.J. Balan, G.S. Patience, J.L. Dubois, Industrial and Engineering Chemistry Research 49 (2010) 1050–1056.
[12] M. Slinn, K. Kendall, C. Mallo, J. Andrews, Bioresource Technology 99 (2008) 5851–5858.
[13] S.J. Yoon, Y. Choi, Y. Son, S.H. Lee, J.G. Lee, Bioresource Technology 101 (2010) 1227–1232.
[14] L. Liu, X.P. Ye, J.J. Bozell, ChemSusChem 5 (2012) 1162–1180.
[15] Y. Mu, Z.L. Xiu, D.J. Zhang, Biochemical Engineering Journal 40 (2008) 537–541.
[16] M. Gonzalez-Pajuelo, J.C. Andrade, I. Vasconcelos, Journal of Industrial Microbiology and Biotechnology 31 (2004) 442–446.
[17] G. Kaur, A.K. Srivastava, S. Chand, Biochemical Engineering Journal 64 (2012) 106–118.
[18] S. Papanikolaou, S. Fakas, M. Fick, I. Chevalot, M. Galiotou-Panayotou, M. Komaitis, I. Marc, G. Aggelis, Biomass and Bioenergy 32 (2008) 60–71.
[19] T. Ito, Y. Nakashimada, K. Senba, T. Matsui, N. Nishio, Journal of Bioscience and Bioengineering 2005 (2005) 260–265.
[20] G. Sabourin-Provost, P.C. Hallenbeck, Bioresource Technology 100 (2009) 3513–3517.
[21] R.D. Ashby, D.K.Y. Solaiman, T.A. Foglia, Journal of Polymers and the Environment 12 (2004) 105–112.
[22] M. Henkel, M.M. Müller, J.H. Kügler, R.B. Lovaglio, J. Contiero, C. Syldatk, R. Hausmann, Process Biochemistry 47 (2012) 1207–1219.
[23] M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, Journal of Catalysis 268 (2009) 106.
[24] M. Tudorache, A. Negoi, L. Protesescu, V.I. Parvulescu, Applied Catalysis B: Environmental, 2013, http://dx.doi.org/10.1016/j.apcatb.2012.12.033
[25] M. Tudorache, L. Protesescu, S. Coman, V.I. Parvulescu, Green Chemistry 14 (2012) 478–482.
[26] M. Tudorache, L. Protesescu, A. Negi, V.I. Parvulescu, Applied Catalysis A: General 437–438 (2012) 90–95.
[27] E.Y. Lee, K.H. Lee, C.-H. Park, Bioprocess and Biosystems Engineering 33 (2010) 1059–1065.
[28] M. Verziu, B. Cojocaru, J. Hu, R. Richards, C. Ciuculescu, P. Filip, V.I. Parvulescu, Green Chemistry 10 (2008) 373–381.
[29] S. Al-Zuhair, F.W. Ling, S.J. Jung, Process Biochemistry 42 (2007) 951–960.
[30] H. Jung, Y. Lee, D. Kim, S.O. Han, S.W. Kim, J. Lee, Y.H. Kim, C. Park, Enzyme and Microbial Technology 51 (2012) 143–147.
[31] A.M. Brzozowski, U. Derewenda, D.M. Lawson, J.P. Turkenburg, F. Bjorkling, B. Huge-Jensen, S.A. Patkar, L. Thim, Nature 351 (1991) 491–494.
[32] J.J. Shangguan, Y.-Q. Liu, F.-J. Wang, J. Zhao, L.-Q. Fan, S.-X. Li, J.-H. Xu, Applied Biochemistry and Biotechnology 165 (2011) 949–962.
[33] Z.-Y. Zheng, J.-K. Yang, Y.-J. Yan, Chinese Journal of Biotechnology 23 (2007) 96–100.